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REVIEW

# Formation of Binder-Free Composites Based on Natural Materials: Structure, Mechanisms, and Prospects for Chemical Modification

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**ABSTRACT:** Binder-free lignocellulosic boards and molded composites are gaining momentum as low-emission alternatives to conventional wood-based panels because they exploit intrinsic self-bonding of biomass under hot pressing. This review critically analyzes structure-formation pathways in binder-free composites, focusing on (i) thermo-mechanical softening and flow of lignin as a natural adhesive phase, (ii) auto-hydrolysis of hemicelluloses generating organic acids and reactive furanic intermediates, and (iii) subsequent condensation and crosslinking reactions that consolidate the network. We compare process routes historically associated with Masonite-type fiber processing and Lignoplast-type direct compaction, highlighting how moisture, temperature, pressure, sealing degree, and particle morphology govern bond development and dimensional stability. Particular attention is paid to chemical activation strategies (oxidants, nitrogen-containing reagents, and reactive bio-based systems) that tune lignin mobility and reactivity, enabling milder pressing and improved water resistance. We outline research gaps linking chemical transformations to macroscopic performance, and propose future directions including *in situ* monitoring, quantitative structure-property models, and activation chemistries compatible with circular and compostable product concepts.

**KEYWORDS:** Binder-free composites; self-bonding; lignin activation; hot pressing; steam explosion; lignocellulosic composites; moisture sensitivity

## 1 Introduction

Humanity faces major challenges in shifting national economies from dependence on primary natural resources to the efficient utilization of secondary raw materials. To address this challenge, researchers propose developing biorefining technologies for plant resources and improving the recycling of lignocellulosic secondary raw materials.

A key requirement for secondary raw materials is their stable availability or recoverability in large quantities at low cost. These factors contribute to the increased competitiveness of secondary raw materials compared to virgin ones.

To enhance competitiveness and reduce production costs, various technological solutions have been proposed. Specifically, plant biomass that meets the following criteria—easy availability (abundance) and high reproducibility—is being used as a raw material for the production of composite materials. Currently,

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various approaches are being explored to utilize lignocellulosic feedstocks, such as crushed wood waste (sawdust, shavings) and fractionated agricultural residues (husks, shives, fibers).

Recent technologies allow lignocellulosic biomass to be converted into composites for multiple applications without synthetic binders. Products derived from plant biomass are readily biodegradable and environmentally benign.

These materials are commonly referred to as binder-free composites (BFC), that is, composite boards produced without synthetic resins. Despite the various approaches to producing BFC, the conditions remain unchanged: hot pressing in closed molds (piezothermal processing) of lignocellulose-containing raw materials in a sealed space. Under these conditions, the lignin-carbohydrate complex is transformed through polycondensation and polymerization reactions, resulting in the formation of a cross-linked and monolithic material with high physical and mechanical properties.

One of the key advantages of plant-based BFC is their ability to undergo hydrolytic and microbiological degradation in the natural environment, thanks to the absence of a synthetic binder or matrix polymer. Consequently, these materials are fully biodegradable and compostable.

Improving BFC production through hot pressing in closed molds requires prior chemical modification of the feedstock. Modifiers such as urea, hydrogen peroxide, and hexamethylenetetramine (urotropine) are widely used for the chemical modification of lignocellulose-containing feedstocks to produce BFC.

Each modifier interacts differently with the specific components of plant materials (coniferous and deciduous wood, herbaceous plants). The purpose of this chemical modification is to activate lignin by exposing its functional groups, which allows it to act as an internal binder in the lignin-carbohydrate complex (LCC).

The mechanisms of BFC structure formation and the interaction of modifiers with plant lignin of various origins are currently poorly understood. Establishing patterns of BFC structure formation based on various lignocellulose-containing raw materials using chemical modifiers will allow us to influence their physical and mechanical properties and achieve a more "milder" production process.

Literature search strategy (and inclusion criteria).

The review is based on a structured search in Scopus, Web of Science, and Google Scholar (last accessed: February 2026). Search strings combined keywords such as "binderless board", "binder-free composite", "self-bonding", "hot pressing", "steam explosion", "lignin activation", "lignin condensation", and "lignin-carbohydrate complex (LCC)". We prioritized peer-reviewed journal articles and authoritative reviews in 2015–2026, with emphasis on 2021–2026 to reflect recent developments. Records were screened by title and abstract; inclusion required explicit processing conditions (temperature/pressure/moisture/time and/or pretreatment severity) and at least one measurable outcome (internal bond, bending strength/modulus, thickness swelling, water absorption, or durability indicators). Patents and historical sources were retained only to document origin of process concepts.

Masonite-type routes rely on fiber generation under steam/thermo-mechanical conditions prior to consolidation; bond development is often enhanced by hydrothermal chemistry and surface redistribution of lignin on fibers. Lignoplast-type routes emphasize direct compaction of particles/fibers in closed or semi-closed tooling, where sealing degree and *in situ* acidity strongly affect auto-hydrolysis and subsequent condensation chemistry. In practice, both routes converge to shared drivers—lignin softening/flow, hemicellulose-derived reactive intermediates, and pressure-enabled contact formation—but differ in how pretreatment determines morphology and chemical readiness [1].

## 2 Developing Binder-Free Composite Materials: Current Approaches

In 1924, William H. Mason patented a process for producing a material known as Masonite [2]. This material was produced by crushing wood chips and saturating them with steam under pressure. The fibers were formed into boards on a mesh, then pressed and heated to produce a smooth, polished product. In Europe, interest in this technology grew in the 1950s–60s, following the work of R. Runkel, W. Klauditz, and others [3]. In Europe, this material was known as Lignoplast, and the method–pressing wood or plant material without binders and without pre-treatment–became known as the Lignoplast process.

Thus, all methods of producing BFC can be broadly classified into two main groups (based on the technologies Masonite [2] and Lignoplast [3]):

1. By hot pressing: direct pressing of lignocellulosic raw materials in closed or semi-closed molds, pressing between heated parallel plates (with or without spacers), pressing in metal trays, or extrusion pressing [4–6].
2. According to the degree of pre-treatment of lignocellulosic raw materials: pressing a molding material that has undergone preliminary modification intended to enrich it with products of activation and decomposition of organic molding material and polymerization or polycondensation reactions:
   - Mechanical—due to hydrodynamic destruction of the polymer—cavitation of wood molding materials [7,8];
   - chemical-mechanical—due to the hydrolysis of weak bonds in the matrix of plant biomass and mechanical loosening of solid raw materials with a sharp drop in pressure—explosive autohydrolysis [9,10];
   - biological—transformation of lignocellulosic components by microorganisms or enzymes, resulting in biodegradation of the substrate [11,12];
   - physical—due to the destruction and change in the structure and chemical composition of the raw material components—heat treatment of the original raw material [13,14];
   - chemical—by introducing both low-molecular and high-molecular chemical substances—modifiers—directly into the press composition [15,16].

More extensive research has focused on composites produced using Masonite technology, particularly regarding the influence of raw material types, pre-treatment conditions, and pressing parameters, which are primarily related to the study of the influence of the types and characteristics of the initial raw materials [17–21], pre-treatment conditions, and pressing parameters [22–25] on the physicochemical properties of the material obtained by this method. Recent reviews provide consolidated comparisons of routes, feedstock effects, and scale-up constraints [1].

Alternative approaches, such as extrusion [26,27] and injection molding, are also being actively investigated [28].

A new technology attracting attention is the Circular Lignin-Polysaccharide Board (CLIPboard) concept—wood-based composites with bio-additives. CLIPboard is produced by hot pressing mixtures. The composition includes plant filler (wood particles, 90%) and bio-additives (sodium lignin sulfonate, 5%, and corn starch, 5%) [29].

Another promising approach involves the use of thermoplastic starch plasticized with suitable agents to produce compostable disposable products [30]. However, despite their advantages, thermoplastic starches have notable limitations, including low strength and high moisture sensitivity. To improve mechanical properties, plant fillers are often added [31].

Various lignocellulosic feedstocks have been considered for binder-free composites, including:

- woody biomass (softwood and hardwood) as fibers, sawdust, shavings, bark, and mixed wood residues used either directly or after thermo-mechanical/hydrothermal pretreatment [24,32–36];
- non-woody biomass, including agricultural residues, straws, husks, and other lignocellulosic by-products [37–40], as well as agro-industrial residues and fibre-rich plant materials [41–44], often requiring pretreatment to improve self-bonding and moisture stability.

In addition to "pure" biomass, binder-free composites have been explored using cellulose-rich or lignin-rich fractions and related process by-products [45]. High-performance binderless boards from *Broussonetia papyrifera* trunk have been reported [46]. Studies have also addressed lignin–carbohydrate complex evolution during autohydrolysis [47] and binderless hot pressing of hot-compressed-water-treated rice husk [48]. Interfacial effects of lignin–carbohydrate complexes on cellulosic substrates have been discussed [49], alongside binderless self-densified lignocellulosic boards and broader lignin-based composite applications and stabilization strategies [50–52].

Table 1 summarizes representative process routes, feedstock, pretreatment, pressing window, and typical outcomes reported for binder-free boards and molded composites.

**Table 1:** Representative process routes for binder-free boards and molded composites.

| Feedstock (Example) | Pretreatment/Route | Pressing Conditions (Typical) | Dominant Bonding Drivers | Typical Outcomes (Qualitative) | Key Limitations | Ref. |
|---|---|---|---|---|---|---|
| Wood particles (oak/poplar/spruce) | Steam explosion (severity tuned) | Hot pressing (moisture-controlled) | Hemicellulose auto-hydrolysis + lignin redistribution/condensation | Improved internal bond and dimensional stability vs. untreated (species-dependent) | Energy intensity; feedstock variability | [53] |
| Wood particles/fibers | Thermally modified wood feedstock | Hot pressing; moisture-dependent | Increased compressibility + lignin mobility | Feasible binderless boards; process window sensitive to moisture and temperature | Moisture sensitivity; process control | [54] |
| Fibers (construction boards) | Thermo-mechanical/hydrothermal routes (reviewed) | Hot pressing (various) | Lignin softening/flow + chemical crosslinking | Broad feasibility; mechanistic consensus emerging | Scale-up limitations | [1] |
| Reconstructed lignocellulosics | Self-binding mechanism synthesis (review) | Hot pressing (various) | Multi-link mechanism: contact → flow → chemistry → consolidation | Mechanistic framework for interpreting IB/MOR/MOE trends | Water resistance often limiting | [55] |
| Reconstructed lignocellulosics | Self-assembly perspective (review) | Hot pressing (various) | Self-organization + bonding networks | Explains variability; highlights need for quantitative models | Needs standardized reporting | [56] |
| Spruce particles + bio-additives | CLIPboard concept (bio-adhesive) | Hot pressing of wood particles + biopolymers | Waterborne bio-adhesive + circular processing | Demonstrates circular route (not strictly binder-free) | Not fully binder-free; additive supply | [29] |
| Agricultural residues (various) | Network-analysis synthesis (review) | Multiple routes | Mechanism mapping across studies | Identifies gaps and consensus; supports critical discussion | Requires experimental unification | [57] |
| General lignin chemistry | Lignin valorization/chemistry (review) | – | Context for activation and condensation chemistries | Modern lignin pathways and constraints | Tech lignin heterogeneity | [58] |

Note: Abbreviations: IB = internal bond strength, MOR = modulus of rupture, MOE = modulus of elasticity.

As shown in Table 1, the ratios of cellulose, hemicellulose, and lignin vary significantly both among plant forms and in the vegetative and generative organs of a single plant form. For example, in the case of herbaceous plants such as wheat straw, cellulose accounts for 28%–38%, hemicellulose for 24%–39%, and lignin for 15%–18%. This results in a ratio of components of approximately 2:2:1 (cellulose: hemicellulose: lignin). In contrast, conifers such as spruce are characterized by a ratio of approximately 1.7:1:1.2 [59,60].

Moreover, the specific properties of each raw material must also be considered. For example, natural fibers are lignocellulosic materials consisting primarily of cellulose microfibrils embedded in an amorphous matrix of lignin and hemicellulose, as well as other components such as pectin, waxes, and fats [61]. Rice husk is "rich" in silicon dioxide [62], larch sawdust contains the easily hydrolyzed polysaccharide arabogalactan [63], etc.

Lignocellulosic waste partially affected by decay can also serve as a valuable additional source of raw material for BFC production, since composites with high technical properties can be obtained from this waste [18]. Depending on the type, wood affected by rot differs from healthy wood by a reduced content of cellulose and easily hydrolysable substances [64].

Thus, at present, the choice of technology, production conditions, and physical and mechanical properties of BFC depend not only on the type and characteristics of the original lignocellulose-containing raw material (determining its component composition), but also on the methods of its modification, as well as its current state under the influence of various environmental factors.

## 3 The Role of Lignin-Carbohydrate Complex in Binder-Free Composites

Although the chemical composition of lignocellulosic raw materials varies, the primary components remain the same: cellulose, lignin, and hemicellulose. During hydrothermal treatment of plant materials and during hot pressing, significant changes occur in the lignin-carbohydrate complex (LCC) of the original lignocellulose-containing raw material [32].

Studies have shown that the dry glass transition temperatures of lignin, cellulose, and hemicellulose are approximately 200°C, 220°C, and 170°C, respectively. In addition, this reflects the fact that plasticization does not occur at a single fixed temperature—the glass transition temperature is also affected by pressure and humidity [65,66].

The softening temperature of native hemicellulose under dry conditions is high and is about 180°C. Amorphous regions of cellulose behave similarly [65].

Thermogravimetric analysis (TGA) also shows [66] thermal decomposition of hemicellulose and cellulose at temperatures around 300°C. Differences in the microfibrillar structure of hemicellulose and cellulose in softwoods and hardwoods are believed to explain the varying reactivity of cellulose in these species (Fig. 1).

The lignin content of plants varies with their origin and species, which also determines their structural features. For example, softwood lignins have higher glass transition temperatures (138°C–160°C) while hardwood lignins have lower values, in the range of 110°C–130°C under dry conditions [67,68]. In the presence of moisture, lignin softens and becomes viscous at around 90°C. In a softened state, lignin becomes sticky and prone to autoadhesion [68].

During BFC production, typical pressing temperatures of 150°C–180°C soften both hemicellulose and lignin [69]. Lignin is believed to play a crucial role in influencing the thermal reactivity of hemicelluloses in wood [70]. High hemicellulose content in wood species, especially pentosans, accelerates the reaction. Therefore, it is better to use beech, birch, and poplar, which contain large amounts of pentosans, rather than spruce and pine, which have low pentosan content, for the process [71,72].

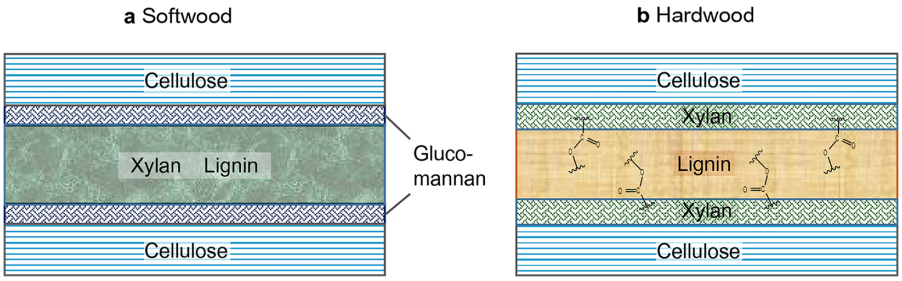


**Figure 1:** Schematic representation of the proposed arrangement of cellulose, hemicellulose and lignin in the cell walls of coniferous and deciduous trees [66].

In the study [73] on the mechanical properties of BFC from miscanthus fiber, obtained by steam explosion using a thermomechanical process using water vapor in a batch reactor, it is concluded that the increase in the stability of the obtained boards (ensuring resistance to deformation and dimensional changes under the influence of external factors) depends on the content of lignin, cellulose, and hemicellulose in the raw material. The results indicate that a reduction in hemicellulose content during processing improves the dimensional stability of the boards.

The authors [74] attribute this phenomenon to decreased board hygroscopicity due to compositional changes, primarily in hemicelluloses. The harsh steam treatment conditions resulted in high dimensional stability, as the fibers lost elasticity through destruction of lignin's aromatic nuclei.

A similar conclusion was reported in [75]. When kenaf stems are treated with hot steam, some of the plant fibers (hemicellulose) are destroyed. The resulting small molecules dissolve in water and transform into sugars and other substances that can act as a natural adhesive.

Other scientists [76] used the same plant material (kenaf pith powder) to produce boards without binders at different pressing temperatures (without steam pre-treatment). The resulting samples were ground into powder and extracted with methanol prior to chemical analysis. To study the chemical changes that occurred, the contents of lignin, holocellulose, and neutral sugars were determined, FTIR measurements were performed, and oxidation with nitrobenzene was used. The results showed that hot pressing caused partial destruction of lignin and hemicelluloses, but the resulting fractions did not contribute to the self-binding of the material.

BFC obtained from technical cellulose by hot pressing in a semi-closed mold has lower strength and water resistance than BFC produced from other types of feedstock. The author attributes this to the high thermal stability of cellulose: it can be heated to approximately 200°C without noticeable decomposition. In contrast, the lignin content in birch wood decreases from 21.5% to 12.5% at 175°C after 1 h of heating, while the pentosan content drops from 27.9% to 6.35%. He also concludes that cellulose is included in BFC as the main filler, giving it increased strength and impact strength [4].

In another study [77], the production of BFC between hot flat-parallel press plates from cotton fiber (cellulose content—87.3%, lignin—2.78%), both pure and with the addition of gum (hydrolyzed and non-hydrolyzed), ended in failure—Instead of a solid monolithic material, only a "cotton pad" was produced.

Article [78] presents the results of a study on the effect of adding lignin to crushed grape branches (Vitis Vinifera) to determine the effect of acid-washed kraft lignin on the physical and mechanical properties of BFC and to explore the possibility of using acid-washed kraft lignin as an alternative to synthetic adhesives. The results showed that BFC produced without lignin exhibited weaker mechanical properties. Adding 15% acid-washed kraft lignin enhanced both mechanical strength and water resistance.

The work [43] indicates that the content of hemicellulose and cellulose decreases with increasing lignin content during hot water pretreatment. However, hot water pretreatment has less effect on cellulose: less than 22% of cellulose was decomposed in wood and herbaceous biomass pretreated at 200°C–230°C [79].

During hot pressing, rising temperatures reduce the moisture content of plant particles, which in turn raises their softening point. For lignocellulosic particles, this temperature increases by approximately 200°C. Initially, composite components retain this form only temporarily, and the duration of this period is determined by their position within the hot press [80].

In a study [76], using Fourier transform infrared (FTIR) spectra, the results showed that parts of the lignin and hemicellulose of kenaf were degraded during the hot pressing process.

Other researchers [74] studied the effect of chemical changes in these materials on their physical and mechanical properties (strength and swelling) using chemical and spectroscopic analysis. The results showed that low-pressure steam treatment (0.6–1.0 MPa) resulted in significant destruction of hemicellulose, lignin, and cellulose. Conventional hot pressing resulted in lower levels of destruction of the chemical components. Kenaf boards produced by hot pressing without any binders demonstrated low bond strength. Thus, the results showed that partial degradation of the three main chemical components of the kenaf core as a result of gentle steam treatment increased the bond strength and dimensional stability of the boards, and made it possible to obtain higher-quality kenaf boards than those produced by hot pressing.

Recycling of crushed BFC particles for their intended purpose is impossible, since the reactivity of lignin and easily hydrolysable polysaccharides is exhausted during the first pressing process. Consequently, when pressed, they exhibit the properties of thermosetting binders [81].

In the work [82], it is proposed to improve the properties of the material using steam explosion. As a result of the explosion, the surface area of the fibers increases, degradation of hemicellulose occurs, the crystallinity of cellulose decreases, and the lignin matrix is destroyed [83]. Drops of lignin are observed on the surface of the fibers [24].

Most studies on BFC production emphasize the central role of lignin in material formation. It is noted that lignin is a natural binder in the composition of lignocellulose-containing raw materials [84].

During thermomechanical processing, wood chips are converted into lignin-coated fibers by shearing wood cells relative to each other along lignin-rich middle plates (middle lamella) [85].

The authors of the study [86] noted that high pressing temperatures have a positive effect on the plasticity of the fibers. The lignin contained in them melts and is distributed evenly, which ensures complete bonding of the fibers and improves their mutual contact.

The authors [87] that at high temperatures, lignin loses rigidity due to dehydration and cross-link formation; therefore, changes in the state of softened lignin are closely related to the chemical transformations taking place and cannot be considered separately from each other.

The authors of [44] suggested that the fluidity of lignin in fibers increases at higher temperatures, which improves the distribution of lignin in fibers and interfiber bonds. Chemical changes in lignin promote “self-adhesion” and improve the properties of the resulting material.

Studies show that fibers can fuse as softened lignin molecules intertwine and bond. Covalent bonds may also be formed in this process [88].

Several research groups [80,89,90] believe that lignin significantly influences the formation of BFC due to its property of softening under high temperature and pressure. Plant Fibers with lignin-rich surfaces bond through the migration of softened lignin molecules, and possibly even through the formation of covalent bonds.

When producing boards without binders based on bamboo, a positive correlation was established between the strength of the boards and the lignin content in the raw material [40].

The authors of [91] report that lignin plays an important role in the production of kenaf-based boards, acting as a natural binder for the fibers. According to the authors, when the fibers are heated, the lignin melts on their surface, and under pressure, the lignin binds the fibers together.

However, other plant material components cannot be isolated from lignin's role, and bonds within the material are formed on the basis of chemical and physical interactions that occur during the hot pressing process between the various components of plant particles or their derivatives [92].

In the work [93] demonstrates that the removal of 80.8% (of the initial state) of easily hydrolysable substances from pine sawdust, and along with them the majority of extractive substances, led to an increase in the bending strength from 10.61 to 12.2 MPa (by 15%), and an increase in water absorption from 16.15% to 23.65% (by 46%) in the resulting BFC. At the same time, the content of easily hydrolysable polysaccharides in the original raw material decreased from 15.27% to 2.93%, i.e., by 5.2 times, and in composites from these materials from 13.74% to 3.08%, i.e., 4.45 times. In composites from different types of wood, the content of easily hydrolysable ones is less than in the original raw material: in coniferous species by 9.25%–13.7%; for aspen by 19.5%; for birch by 41.6%.

A study [94] examined the effects of particle size, moisture content, and heating temperature at a fixed pressure and time on the physical, thermal, and mechanical properties of hemp-based binder-free composites. The composites were produced using a single-step thermoforming process. The results showed that the fine particle composites exhibited the best properties at the optimum temperature of 170°C. The mechanical properties of the resulting composites met the requirements for particleboard. It was also noted that the composites were very sensitive to water: they completely degraded within 5 min upon direct contact with water. This characteristic can be exploited for biodegradability. After the end of the useful life of such a lignocellulosic composite, a fermentation process can be initiated using ligninolytic fungi and enzymes that are involved in the breakdown of the complex and resistant polymer of this material—lignin.

A study [95] examined the potential of coconut husk as a raw material for the production of BFC. The obtained samples were examined using thermal analysis, Fourier transform infrared spectroscopy, and scanning electron microscopy. The mechanical properties, swelling, and water absorption of the BFC were also studied. The pressing temperature strongly influences the physical and mechanical properties of the material. The use of high temperatures allows for the production of a material with increased water resistance (similar to HDF boards). The authors conclude that coconut fiber contains a large amount of lignin, which, under suitable pressure and temperature conditions, can act as a natural binder.

In recent years, numerous methods have been developed to convert wood and agricultural waste into composite products such as panels and molded products based on the extraction and release of the natural component lignin from lignocellulosic materials, which can serve as a binder [96].

From the above, it is clear that lignin is a key component of plant materials for producing durable and water-resistant BFC. During hot pressing treatment, lignin is activated and acts as a binder. Particles of lignocellulose-containing raw materials lose some of their properties, but acquire others, which contribute to their connection [71].

Determining the structural characteristics of lignins of different plant origins, their functional composition, and chemical modification products is becoming particularly important. This primarily concerns reactive hydroxyl groups, which are present in the lignin macromolecule as substituents in aliphatic chains and in the form of phenolic structures, such as guaiacyl, syringyl, and hydroxyphenyl types. Therefore, a

thorough understanding of the functional composition of lignin is a prerequisite for the effective use of lignocellulose-containing raw materials in recycling processes [58,97].

The quantitative values reported in this manuscript (e.g., internal bond strength up to 2.74 MPa with 24 h thickness swelling of 7.4%, and internal bond values on the order of ~2.9 MPa with thickness swelling around ~8%) suggest that the apparent "lignin vs. hemicelluloses" contradiction largely depends on the processing window (moisture level, degree of sealing, pretreatment severity) and the achieved densification.

## 4 Natural Lignins: Chemical Composition, Structure and Properties

Lignin can be classified into two categories: natural (protolignin) and chemically derived forms. Chemical processing yields technical lignins, such as alkaline, sulfonate, and hydrolytic types. Natural lignin is one of the most abundant biopolymers, present in the cell walls of vascular plants [98].

Lignin can be classified into three main groups: softwood lignins, hardwood lignins, and herbaceous lignins. Softwood lignins have been studied in the greatest detail, followed, to a lesser extent, by hardwood lignins. Research on herbaceous lignins remains limited, largely due to their morphological variability across species, habitats, and growth stages [99].

Plant lignin content varies by species, tissue type, developmental stage, and growth conditions, which can also affect lignin distribution within the cell wall and its reactivity during hot pressing [100–104]. Unmodified technical lignins have recently been explored as sustainable binders in structural biocomposites [105].

Lignin classification can also be based on the chemical structure of its monomer units (Fig. 2). Lignins are derivatives of three hydroxycinnamic alcohols—n-coumaric, coniferyl, and sinapyl (monolignols), which differ in the degree of methoxylation [105].

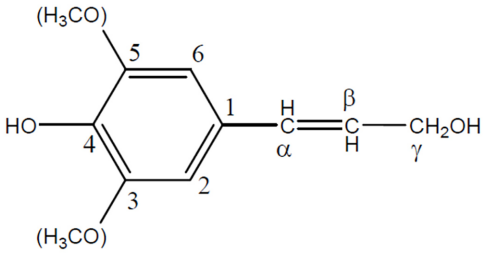


**Figure 2:** Phenylpropane monomer—structural unit of the monomer (methoxyl groups in brackets may be present or absent) [105].

Depending on the presence of methoxyl groups, there are three precursor monomers (Fig. 3) [106]:

(1) n-coumaric alcohol—without methoxyl groups (H)-lignins (hydroxyphenylpropane structure);
(2) coniferyl alcohol—one methoxyl group (G)-lignins (guaiacylpropane structure);
(3) sinapyl alcohol—two methoxyl groups (S)-lignins (syringylpropane structure).

These compounds are precursors of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units—the structural elements of lignin linked by various types of bonds (Fig. 4) [107].

Three main groups can be distinguished: herbaceous lignin, softwood lignin, and hardwood lignin. Depending on the configuration, herbaceous lignin is classified as GSH lignin, softwood lignin is classified as G lignin, and hardwood lignin is classified as GS lignin [108–110].

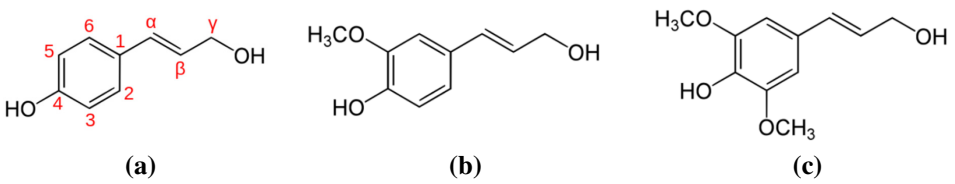


**Figure 3:** Types of lignin monomers [106]: (**a**) (H)-lignins (Coumaric alcohol); (**b**) (G)-lignins (Coniferyl alcohol); (**c**) (S)-lignins (Sinapyl alcohol).

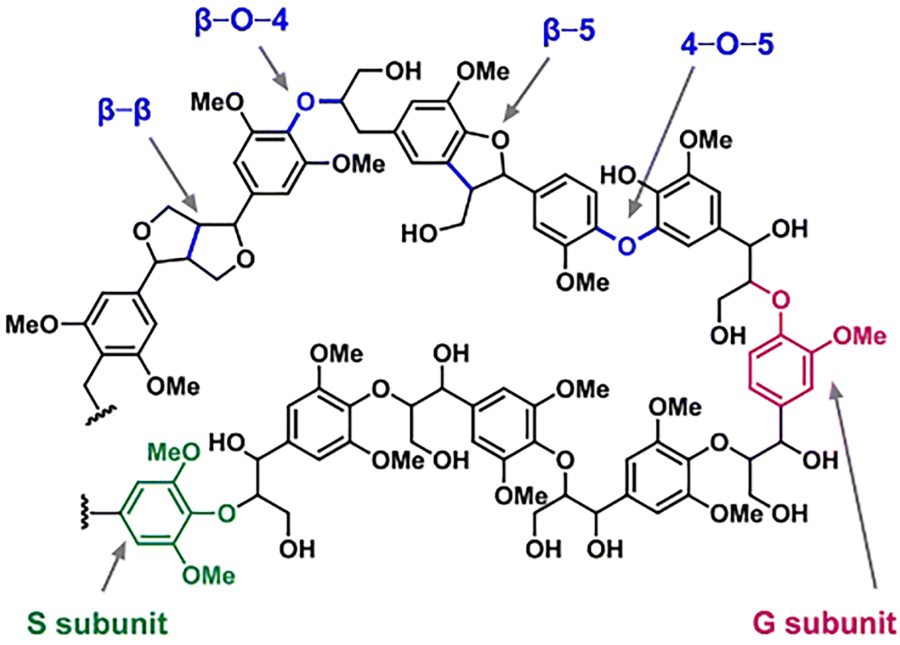


**Figure 4:** Structural model of hardwood lignin [107].

The distribution of structural units among plants of various biological origins is presented in Table 2.

Distribution of structural units of different types for plants of different biological origin in approximate form (S:G:H, %): coniferous species 0 ÷ 1:90 ÷ 95:0.5 ÷ 3.4, deciduous species 50 ÷ 75:20 ÷ 50:traces, herbaceous 25 ÷ 50:25 ÷ 50:10 ÷ 25.These three monomers, linked by C–O or C–C bonds, form a robust and chemically stable polymer [111].

For a long time, it was believed that lignin consisted only of H-, S-, and G-units, but research over the past 20 years has revealed the presence of other monomers, leading to even greater diversity in lignin's physicochemical properties. More than 30 minor monomers are currently known, but most of them are absent from trees [112].

The predominant type of intermonomer bonds in the lignin polymer is the β-O-4 bond, which forms the structures of alkyl-aryl ethers. In addition, the presence of such bonds (and corresponding structures) as β-5 (phenylcoumarans), β-β (resinols), 5-5 (dibenzodioxocines), 5-O-4 (biphenyl ethers), β-1 (spirodienones) was established [113] (Fig. 5, Table 3).

**Table 2:** Ratio of H-, G-, and S-structures for lignin in different plants.

| Plant | Organ, Tissue | H-Structure | G-Structure | S-Structure | Literature |
|---|---|---|---|---|---|
| Larch | wood | 0 | 100 | 0 | [114] |
| Spruce (common) | wood | 0.8 | 99.2 | 0 | [115] |
| Spruce | wood | 5 | 94 | 1 | [116] |
| Pine (radiata) | wood | 0.5 | 99.5 | 0 | [115] |
| Pine | wood | 13 | 86 | 2 | [116] |
| Birch | wood | 3 | 27 | 70 | [117] |
| Oak (cork) | wood | 5 | 72 | 23 | [118] |
| Beech | wood | 4 | 56 | 40 | [116] |
| Bamboo (*Dendrocalamus sinicus*) | trunk | 9 | 35 | 56 | [119] |
| Eucalyptus | bark | 1 | 26 | 73 | [120] |
| Acacia | bark | 5 | 50 | 45 | [120] |
| Spruce | bark | 14 | 86 | 0 | [120] |
| Rye (sowing) | straw | 4.3 | 46.9 | 48.7 | [121] |
| Rice (sowing) | straw | 5 | 71 | 24 | [98] |
| Wheat | straw | 3 | 61 | 36 | [122] |
| Oats (Karen variety) | straw | 12.5 | 48.4 | 39.1 | [123] |
| Sosnowsky's hogweed | stem | 11 | 40 | 49 | [124] |

Lignin contains functional groups such as methoxyl, carbonyl, carboxyl, and hydroxyl groups [125]. All the regularities of chemical reactions of organic chemistry are fulfilled for the functional groups of lignin [113].

In the aromatic ring, the reaction centers for chemical polymerization in the lignin structure are phenolic and aliphatic hydroxyl groups (Fig. 6) [107].

Free radicals formed during the breakdown of lignin–carbohydrate bonds play a key role in polymerization reactions leading to the formation of a cross-linked structure. Radicals can form not only during chemical treatment (acids, alkalis, enzymes), but also during mechanical degradation of wood. The mechanism of radical formation has been studied by many researchers [81,126,127].

Recent studies [128,129] in computational quantum chemistry allow for a detailed study of lignin's active sites and radicals, helping to understand the mechanisms of reactions occurring in lignin. These calculations allow us to determine how various functional groups, such as hydroxyl, aldehyde, and carboxyl, influence lignin's reactivity. They also help explain the role of free radicals, which are formed by the breakdown of lignin-carbohydrate bonds and participate in polymerization reactions that lead to the formation of a network structure.

Quantum-chemical calculations based on density functional theory (DFT) provide insight into the electronic structure of lignin systems, one of the key methods of theoretical modeling, are used to accurately predict the structures, physical and chemical properties of molecules, as well as the interactions of lignin structural units at the molecular level [130].

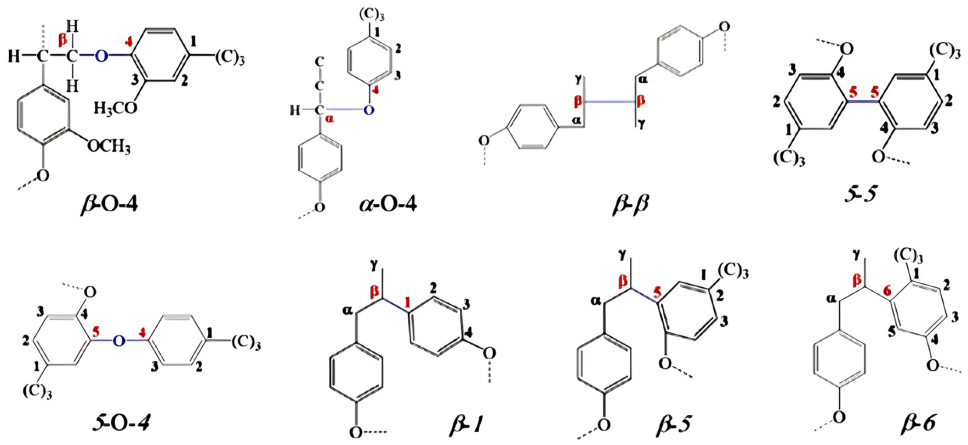


**Figure 5:** Typical intermonomer bonds in lignin [113,131].

**Table 3:** Distribution of intermonomer bonds of different types in lignins isolated from herbaceous plants, coniferous and deciduous forest stands (%) [113,132–134].

| Connection Type | Dimeric Structure | Herbaceous Plants | Hardwoods | Softwoods |
|---|---|---|---|---|
| β-*O*-4 | β-alkyl-aryl ether structures | 69 ÷ 94 | 50 ÷ 65 | 45 ÷ 50 |
| α-O-4 | α-alkyl-aryl ether structures | 11 ÷ 14 | 1 ÷ 8 | 5 ÷ 8 |
| β-5 | Phenylcoumarans | 5 ÷ 11 | 3 ÷ 11 | 9 ÷ 12 |
| 5-5 | Biphenyls and dibenzodioxocines | – | 1 ÷ 5 | 5 ÷ 25 |
| 5-*O*-4 | Biphenyl ethers | – | 6 ÷ 7 | 3.5 ÷ 8 |
| β-1 | Spirodienones | 0 ÷ 2 | 1 ÷ 7 | 1 ÷ 10 |
| β-β | Resinols | 1 ÷ 15 | 3 ÷ 12 | 2 ÷ 6 |

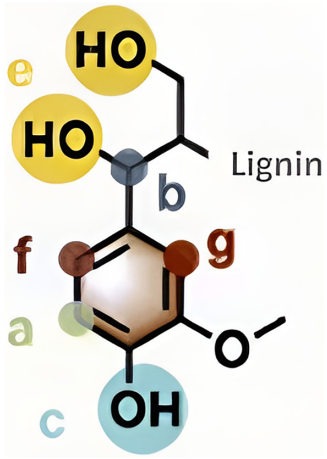


**Figure 6:** Examples of common methods of chemical polymerization of lignin by crosslinking [107]: hydroxymethylation (**a**), sulfonation (**a**), nitration (**a**), azocrosslinking (**a**), methylation (**a**), phenolate (**b**), propylene oxide, polyethylene glycol, polydiglycidyl ether (**c**,**e**), formaldehyde (**f**,**g**).

In the study [135], sinapyl alcohol, p-coumaryl alcohol, and coniferyl alcohol were theoretically investigated. The molecular geometry and molecular structural parameters of the monolignols were determined using the density functional theory (DFT/B3LYP) method with the 6-31G (d, p) basis set. The scaled vibrational frequencies and chemical shifts of the monolignols were also calculated by this method. The ground-state molecular structures of the monolignols were optimized using the Gaussian 09 method.

The three-dimensional LUMO and HOMO plots for monolignols are shown in Fig. 7. The results showed that in sinapyl, coniferyl, and p-coumaryl alcohols, the energy gap values of LUMO and HOMO were 4.62, 4.69, and 4.79 eV, respectively, indicating that charge transfer occurs to a greater extent within the sinapyl alcohols.

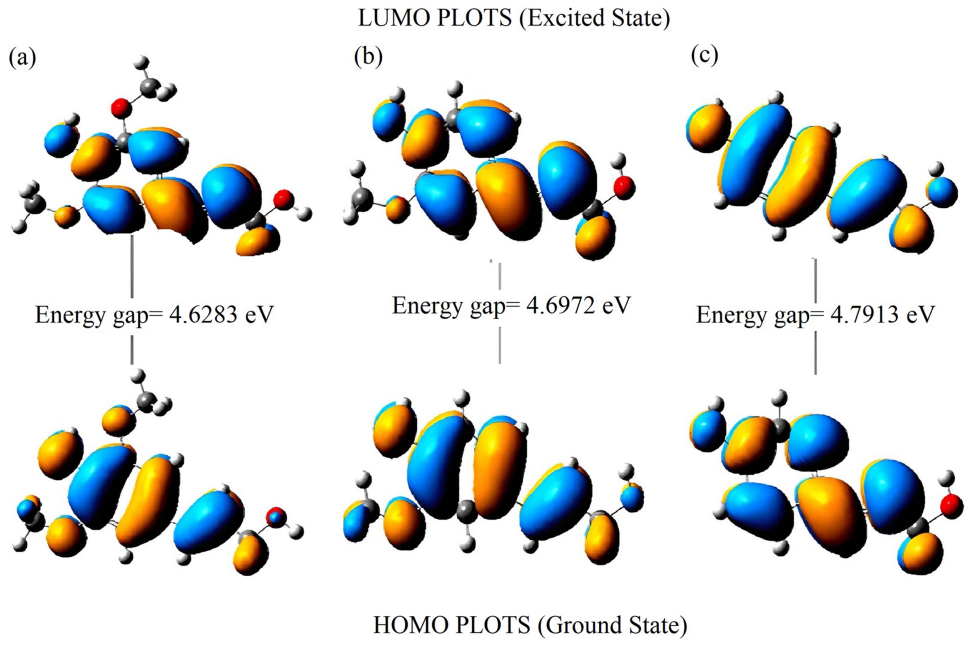


**Figure 7:** Frontier molecular orbitals sinapyl alcohol (**a**), coniferyl alcohol (**b**) and p-coumaryl alcohol (**c**) [135].

The electrophilicity indices of sinapyl, coniferyl, and coumaryl alcohols are 1.647, 1.93, and 2.089, respectively. P-coumaryl alcohol has the highest electrophilicity index. Therefore, it is most prone to participate in electrophilic substitution or addition reactions. Thus, additional methoxy groups decrease electrophilicity by dispersing positive charge, since methoxy groups effectively dissipate the positive charge, reducing the likelihood of electrophilic reactions.

In the work [136], studies were carried out on model compounds of lignin—derivatives of cinnamic alcohols, which are precursors of the structural units of lignin (monolignols): p-coumaric alcohol (I), coniferyl (II), and sinapic (III) alcohols (Fig. 8). Quantum-chemical calculations were also performed using the B3LYP hybrid density functional theory and the restricted Hartree-Fock method in the 6-311 (d, p) basis set. Fig. 8 shows the calculated geometric characteristics of the model compounds.

All model alcohol molecules studied have an aliphatic fragment with a double bond conjugated to an aromatic ring. Consequently, a center of increased electron density appears on the Cβ carbon atom (I = −0.152, II = −0.205, III = −0.194).

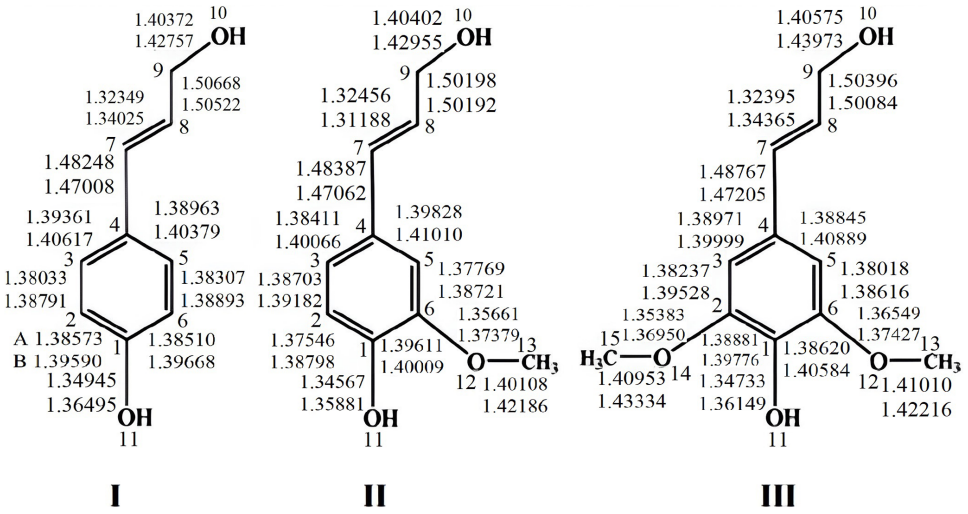


**Figure 8:** Geometric characteristics of cinnamic alcohol derivatives calculated by ARHF/6-311 (d, p) and BB3LYP/6-311 (d, p) methods: (**I**)—coumaric alcohol, (**II**)—coniferyl alcohol, (**III**)—sinapic alcohol [136].

Based on the results of these values, a series of reactivity of carbon and oxygen atoms of the studied molecules in electrophilic and nucleophilic reactions was constructed:

- for coumaric alcohol (I), the only carbon atom C1 has a positive charge; in the series of atoms with negative charges, the reactivity is as follows: C8 > C6 > C2 > C7 > C3 > C5 > C4 > C9 and O10 > O11;
- for coniferyl alcohol (II), respectively, C1 > C6 > C9 and C8 > C13 > C5 > C2 > C7 > C4 > C3, and O12 > O10 > O11;
- for sinapic alcohol (III)—C1 > C6 > C2 > C9 and C8 > C13 > C15 > C5 > C7 > C3 > C4 and O12 > O10 > O14 > O11; for methylconiferyl alcohol (IV)—C6 > C1 > C9 and C8 > C13 > C16 > C5 > C7 > C2 > C3 > C4, and O10 > O11 > O12 [137].

Other scientists, in the article [138], studied the reactivity of these molecules (hydroxycinnamic alcohols: p-coumarol, cinnamic alcohol, and sinapal) using the Fukui function within the framework of density functional theory (DFT).

The studied structures were constructed and optimized using *ab-initio* calculations in PC-GAMESS (ver. 7.0). Conformational analysis to obtain equilibrium geometries was performed using DFT calculations with the B3lyp hybrid density functional (which includes the electron correlation effect), using the 6-31G basis set.

To study the reactivity of the compounds under study, a comparative study of their nucleophilic, electrophilic, and free-radical properties was conducted. The analysis was conducted using quantum chemical modeling based on the Fukui function.

Isocontour maps of the distribution of Fukui function values for the free-radical form were obtained, illustrating the distribution of reaction centers relative to reactants with different levels of electron density. These regions indicate the most likely sites for the formation of new chemical bonds.

Fig. 9 shows a map for the electrophilic form of the Fukui function (f − (r)). This form characterizes the soft regions of monolignol molecules, which are capable of donating electrons, and exhibits increased reactivity toward acceptors with low electron density. Thus, this picture allows us to identify key interaction points and reaction mechanisms occurring in the systems under study.

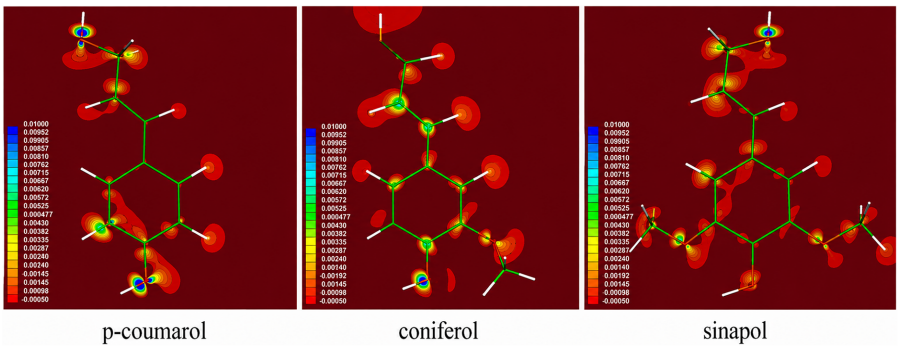


**Figure 9:** Isocontours of the electrophilic form of the Fukui function f(r) [138].

The most reactive sites for reactions involving free radicals were found to be the carbon atoms in the β-position in p-coumarol and sinapol molecules, while the regions around the carbon-oxygen bond of the phenoxyl (hydroxyl) group were the most reactive in coniferol [138].

Key research areas include the structure and properties of lignin molecules, the initial stages of polymerization, and chemical reactions of degradation and modification. Computational chemistry models the formation of free radicals and conformational changes. The DFT method is used to analyze reaction energy profiles and predict the stability of intermediate compounds. Chemical transformations under the influence of acids, alkalis, oxidizing agents, and reducing agents are modeled, and the enzymes catalyzed by lignin conversion are studied [139–141].

## 5 Mechanisms of Structure Formation in Binder-Free Composite Materials

To date, no unified concept describes the mechanism of binder-free composite formation from lignocellulosic raw materials. This is due to the complexity of the chemical processes involved and the absence of simple chemical formulas for the components of lignocellulosic raw materials. Furthermore, this is due to differences in the methods of material production, the differences in the original plant material, its characteristics (physical form, moisture content, degree of grinding, etc.), the conditions of hot pressing (pressure, temperature, holding time, degree of process sealing, cooling, and pressure release rate), and so on.

Researchers, using various methods and accounting for these differences, have proposed multiple mechanisms for the formation of composite structures without the use of binders from lignocellulose-containing raw materials. Their conclusions are based both on established patterns, supplemented by their own experimental data, and on an analysis of specific areas of the experimental results obtained. Furthermore, some researchers highlight the different roles of chemical components of the raw materials, such as lignin, cellulose, and hemicellulose.

As noted above, most studies emphasize the crucial role of free radicals, which act as potential centers for lignin cross-linking reactions [142,143].

However, some argue that the presence of free radicals in lignin degradation products does not necessarily indicate high reactivity [144]. The activity of these radicals is limited by steric factors, and their potential reactivity can be realized only under appropriate activation conditions.

The mechanism of the process of formation of BFC using the “Masonite” technology was proposed as a result of the experiments carried out [75,76,145,146]. These studies involved a series of chemical analyses aimed at examining the chemical changes in LCA during the production of BFC from kenaf pith during hot pressing, both with and without steam pre-treatment. The results showed that water-soluble components are

formed during hemicellulose hydrolysis, as well as some extractives and volatile decomposition products, in a process in which steam pressure and pressing play an important role in the degree of decomposition [75].

During hot pressing treatment of plant materials (150°C–250°C, under high pressure and limited moisture), several concurrent chemical processes take place. Proposed processes include lignin–furfural bond formation, lignin condensation, and furfural self-polymerization [41,84,142]. Under these hot pressing conditions, hemicelluloses (particularly xylans) decompose, releasing acetic acid, which catalyzes further hydrolysis. During the hydrolysis process, acetic acid, formic acid, and cinnamic acid are formed, and some sugar is released, and some furfural products are formed from this hydrolyzed hemicellulose [147].

Pentoses undergo acid-catalyzed dehydration to form furfural, a key intermediate. In an aqueous environment, pentosans are converted to pentoses, which, upon elimination of water, are converted to furfural via reaction [148] (Fig. 10).

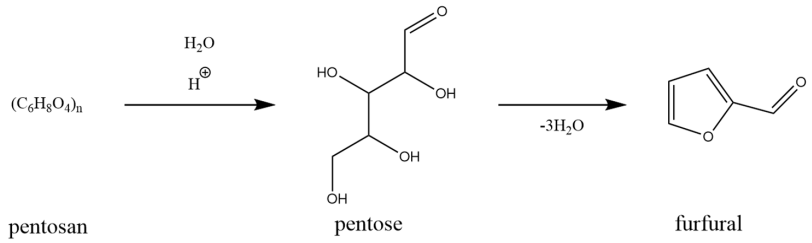


**Figure 10:** Scheme of the reaction of dehydration of pentoses in aqueous media [149].

Hot pressing induces autohydrolysis of hemicelluloses [150], mainly xylans. The proposed mechanism is acid-catalyzed dehydration of xylose, in which substitution of the protonated C-2 hydroxyl group leads to the intermediate product 2,5-anhydride, which dehydrates to furfural (Fig. 11) [151].

Further polycondensation reactions may occur, including:

- lignin—lignin [41];
- lignin—furfural [84];
- furfural—furfural [142].

According to the works [137,152,153], the polycondensation of lignin components proceeds according to the proposed scheme (Fig. 12).

Under these conditions, lignin softens to a viscous state, fills interfiber spaces, and undergoes partial hydrolysis into phenolic fragments [154].

The diagram shows the mechanism of condensation of lignin fragments, which occurs under the elevated temperature and acidic environment typical of hot wood pressing processes. The side chain of the lignin fragment, containing an alcohol group (CHOH in the diagram), is protonated in an acidic environment, after which it loses a water molecule. This leads to the formation of a benzyl carbocation—a stable electrophilic center activated by conjugation with the aromatic ring.

The resulting carbocation reacts with another lignin fragment, attacking its aromatic ring in the ortho or para-position relative to the phenolic group. This results in electrophilic aromatic substitution, forming a new carbon-carbon bond between the two lignin units. Subsequent proton abstraction restores the aromatic system, completing the reaction.

During thermal hydrolysis of hemicellulose, furfural (furan-2-carbamate) is formed, which in an acidic environment is protonated at the aldehyde group and converted into an active electrophilic center (Fig. 13), forming a -CH(OH)- bridge [55].

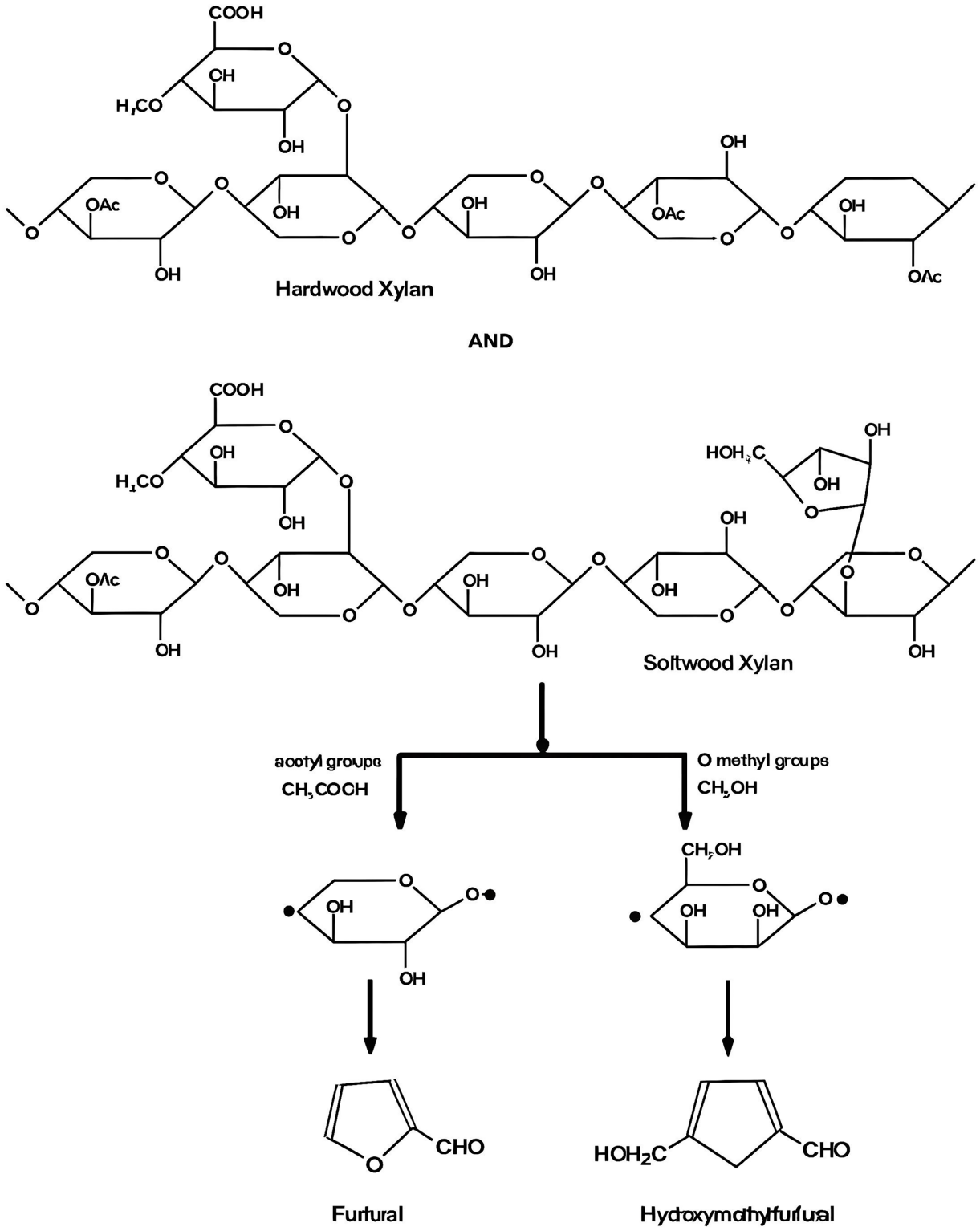


**Figure 11:** Scheme of the reaction of formation of furfural and 5-hydroxymethylfurfural from xylose [151].

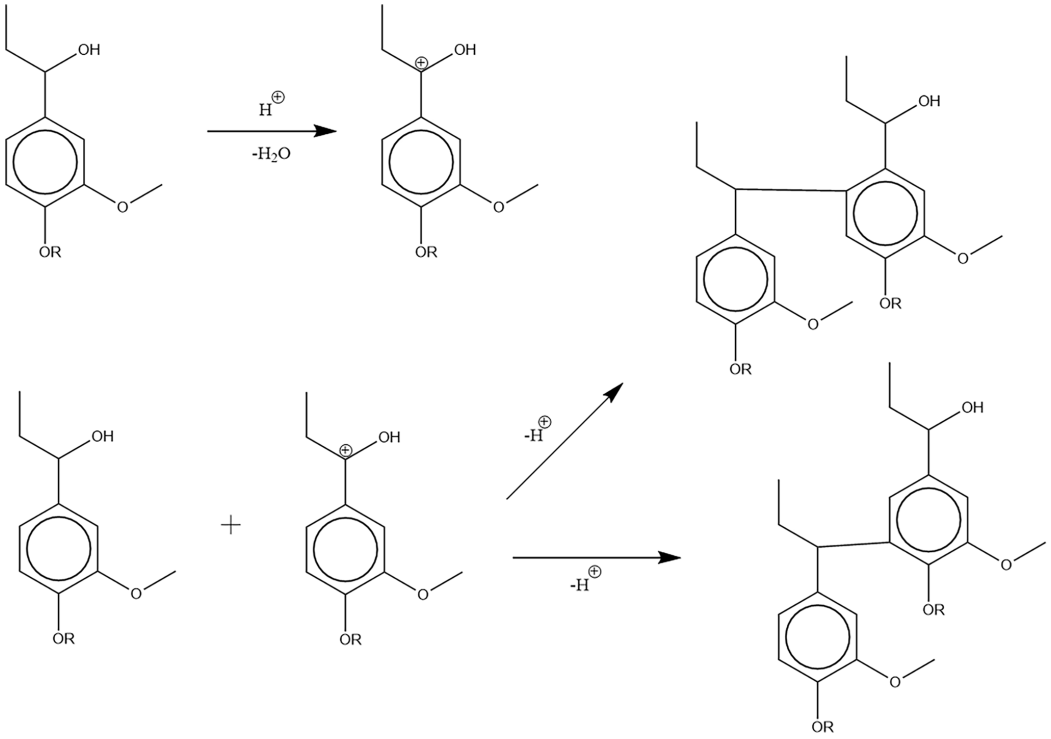


**Figure 12:** Scheme of lignin polycondensation [155].

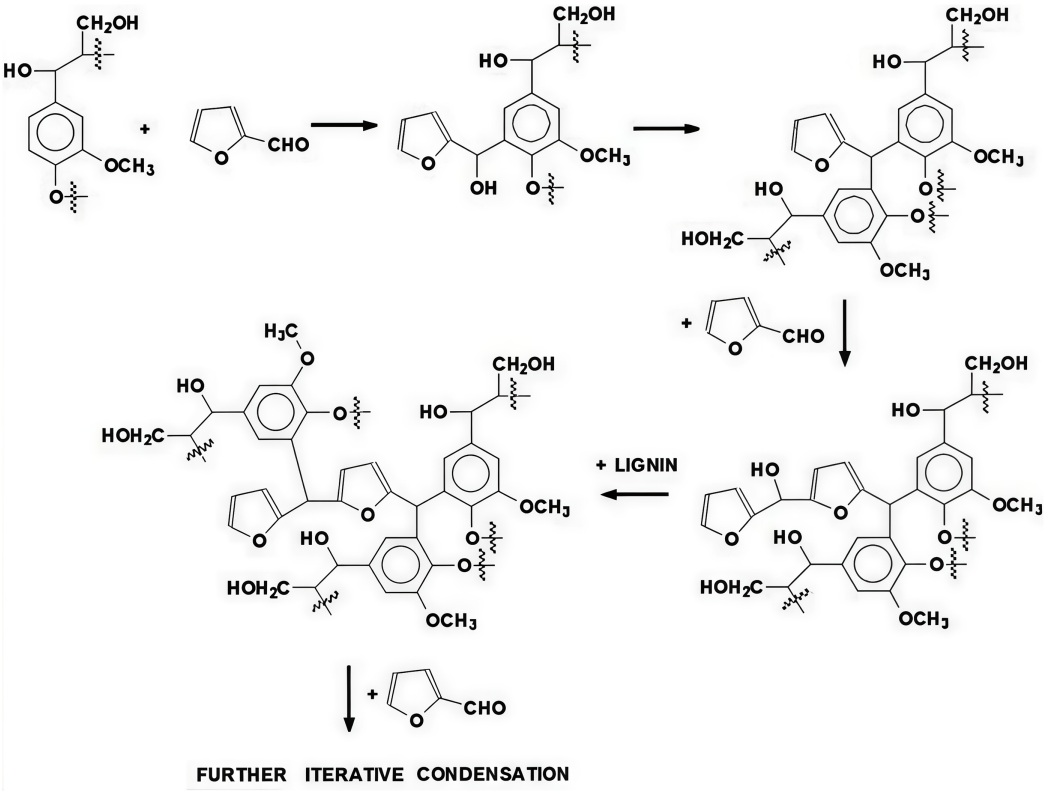


**Figure 13:** Scheme of polycondensation of lignin with furfural [55].

The loss of a water molecule results in the formation of a carbonium ion at the α-carbon of the furan ring. This ion attacks the aromatic ring of lignin at the ortho position relative to the oxygen-bridged phenylpropane units of the lignin or the phenolic hydroxyl group, where the electron density is greatest.

As a result, a methylene bridge (–$CH_2$–) forms between the furan unit and the aromatic ring of lignin, or, depending on the conditions, the furan ring is retained and a furano-aryl bridge is formed. After the proton is removed, the aromatic structure of the ring is restored, completing the electrophilic substitution process.

Together, these reactions yield a robust polymer network.

Furfural–furfural polycondensation may also occur, although its contribution to strength development remains uncertain [55].

In general, a possible scheme for the formation of BFC using the Masonite technology is shown in Fig. 14.

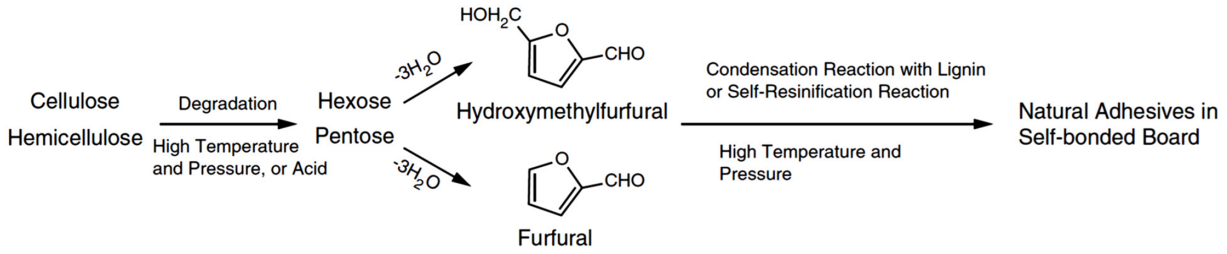


**Figure 14:** Potential mechanism of self-bonding in binder-free composites [142].

The mechanism of the process of formation of BFC using the Lignoplast technology was proposed on the basis of literary data [4,6] and the studies carried out on the transformation of plant raw materials (using wood as an example) during its hot pressing using the differential scanning calorimetry method [156,157].

In the first stage, plant material is subjected to high pressure and rising temperature, leading to compaction and deformation. As the pressing material heats up, moisture evaporates or remains in a liquid form with a high heat content.

In the second stage, under the influence of heat, heated moisture, and its vapor, easily hydrolyzed elements of plant material, such as hemicelluloses, gums, and pentosans, undergo hydrolysis to form monosaccharides. With further heating, the monosaccharides break down into water and furfural, formic acid, and high-molecular-weight humic substances. Concurrent pyrolysis leads to the formation of acetic acid.

The resulting formic and acetic acids accelerate further hydrolysis of the lignocellulose-containing raw material, followed by the decomposition of the monosaccharides into furfural and other products.

During the pyrolysis of lignin, resins, and other components of lignocellulose-containing raw materials, total phenols are formed in significant quantities. During the hot-pressic treatment of organic material in a confined space, other reactive products are also formed, such as hydroxymethylfurfural, formaldehyde, ketones, acetaldehyde, and others. Lignin increases its reactivity during hydrolysis.

Using the DSC method, it was established [157] that both in open and sealed spaces, under the influence of an acidic environment formed by the released simple organic acids, the destruction of these components to simple organic compounds occurs as a result of hydrothermal hydrolysis.

The thermohydrolytic degradation of wood components under elevated temperature, pressure, and moisture proceeds according to the following reactions, i.e., they correspond to the process of hydrolysis of lignin, a carbohydrate complex, and the easily hydrolyzed part of cellulose (1), (2), (3) (Fig. 15).

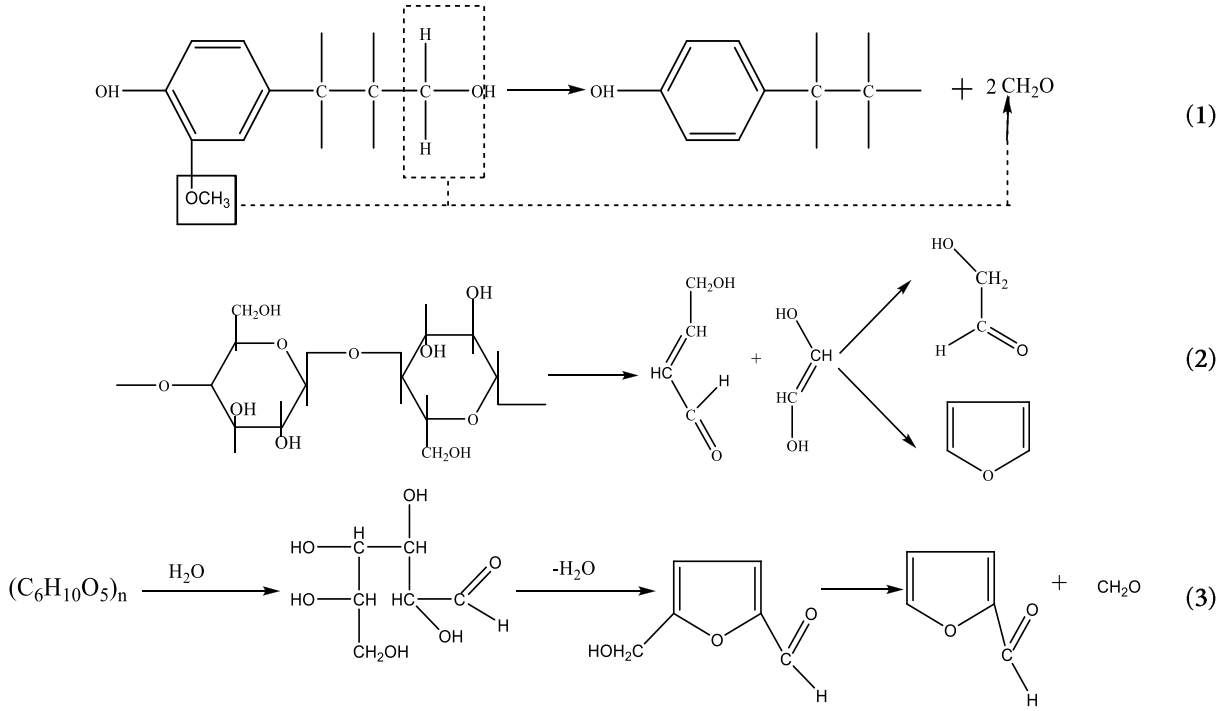


**Figure 15:** Destruction of wood components under the influence of temperature, pressure and moisture [157]: (**1**) structural unit of lignin → formaldehyde. (**2**) Structural unit of cellulose → glycolaldehyde and furan. (**3**) Polysaccharide → hydroxymethylfurfural → dihydroxymethylfurfural → furfural and formaldehyde.

The studies conducted using the DSC method show that the best model describing the process of hydrothermal hydrolysis of wood is the process of type A–1 → B. Since the process is catalyzed by acids that are formed during the pyrolysis of wood, as well as due to the presence of resin acids contained in the extractive substances, this is an n-order reaction with autocatalysis.

In the third stage, the compaction process of the molding material continues. In the sealed mold, decomposition products of organic material undergo polycondensation and polymerization under the influence of elevated temperature, pressure, and catalysts released from the wood itself (acetic, formic, and other acids), forming synthetic resins and other binders.

Polycondensation of wood component fragments with multifunctional wood components can be described by reactions (4), (5), (6), and (7) (Fig. 16).

The calculations performed using the software package NETZSCH (thermokinetics) show that the most reliable model is the process of the type B–2 → C (n-order reaction).

Under pressure, the binders spread over filler particles in the molding material as ultra-thin films. The smaller the particle size and the greater the pressing pressure, the thinner these films. Under the influence of heat, the adhesive layers of synthetic resins undergo a process of polycondensation or polymerization until they become board. During cooling, the monolithic structure of the composite is formed.

Cellulose largely retains its structure and serves as a reinforcing filler rather than a binder. Quantitatively, it undergoes minor changes, and the BFC acts as a reinforcing filler [4,6].

As shown above, the mechanism of formation of BFC is a complex and multifactorial process, including a number of successive stages, each of which is characterized by specific chemical reactions and physical changes.

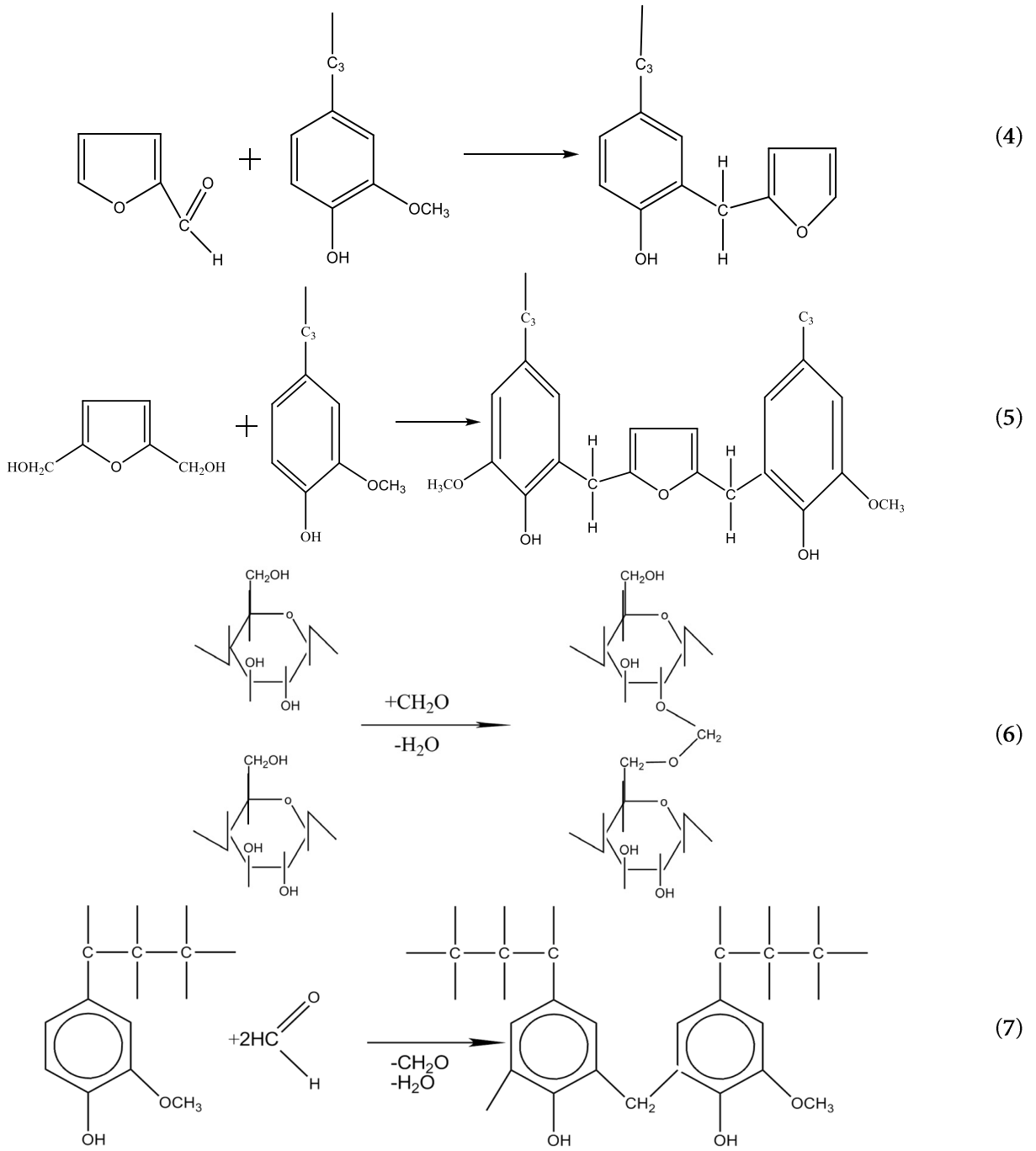


**Figure 16:** Polycondensation of simple fragments of wood components with multifunctional wood components [157]: (**4**) furfural and lignin → fragment of thermosetting resin No. 1. (**5**) Dioxymethylfurfural and lignin → fragment of thermosetting resin No. 2. (**6**) Cellulose and formaldehyde → fragment of cross-linked polymer No. 1. (**7**) Lignin and formaldehyde → fragment of cross-linked polymer No. 2.

## 6 Chemical Activation of Lignin for Binder-Free Composites

During modification of lignocellulosic material (mechanical, physical, chemical, biological, or combined), both the whole matrix and its individual components may be affected.

The positive effect of various chemical modifiers—both low- and high-molecular-weight—on the intensification of BFC formation processes has been established. Each modifier has its own mechanism of interaction with the component composition of lignin-cellulose-containing raw materials.

As shown above, lignin of the original raw material plays the most critical role in BFC formation, but due to its complex structure, it requires pre-activation to enhance its reactivity.

One common approach to lignin activation is intensive hydrolysis of lignocellulosic material using water or acids at elevated temperatures. This process removes the hemicellulose portion, resulting in an increase in the lignin-to-cellulose ratio compared to the original value in lignocellulosic materials, which in turn enhances the efficiency of self-crosslinking [95].

In addition, chemical modification of lignin can reduce its glass transition temperature, for example through sulfonation or esterification [158], thereby increasing its fluidity and improving the pressing process.

Chemical modification of plant materials with various reagents (chlorine, ammonia, monosulfite, caustic soda, dilute sulfuric or hydrochloric acids, and other organic and inorganic chemicals) is performed to partially hydrolyze the molding feedstock and enrich it with native binders. A number of studies have been devoted to the introduction of chemical modifiers to improve the properties of BFC [4–6].

Ammonia is widely used to improve the operational and technological properties of pressed wood and composites based on small wood particles.

Ammonia treatment has been reported to improve the processability of lignocellulosic particles and can enhance consolidation and moisture response during hot pressing. The magnitude of the effect depends on ammonia concentration and processing conditions [159].

The acidity of the initial wood press composite strongly influences the properties of the resulting wood-based composites. The acidity of the plant-based raw material can be increased to the required level by adding mineral or organic acids [4–6].

An acidic environment can also form directly during hot pressing, provided the system is fully sealed. Heating wet wood to 100°C–120°C results in the formation and release of water vapor and organic acids (primarily acetic acid), which lowers the pH of the environment. This is why hydrolytic reactions during hot pressing are autocatalytic [147,156].

Transformations of the chemical composition and structure of the feedstock were assessed using fractional analysis and scanning electron microscopy (SEM). Intensive pre-treatment resulted in the separation of fibrous structures, creating conditions for the formation of intermolecular compounds and subsequent composite fabrication. Even small amounts of acid substantially altered the material's microstructure. Improvements in the physical and mechanical properties of the composites were observed with increasing pre-treatment until peak strength was reached, after which further increases in the degree of treatment began to negatively impact mechanical properties.

In another study [160], lignin-carbohydrate raw materials (aspen, fir, pine, birch, poplar, reed) were reacted with monochloroacetic acid (MCAA) to detect the presence of carboxymethyl groups for the purpose of replacing cellulose to produce binder-free board materials. The IR spectra of all the obtained samples showed a clear absorption band in the region of 1595–1600 $cm^{-1}$, which corresponds to the stretching vibrations of the carbonyl group in the carboxyl radical in the salt-bound (COONa+) state. The intensity of the absorption band of hydroxyl groups in the region of 3400–3600 $cm^{-1}$ is somewhat reduced, compared to the absorption in the same region for the original wood. It was concluded that plant material interacts with MCAA, and the free hydroxyl groups of all lignin-carbohydrate raw materials components (cellulose, lignin, hemicelluloses) are obviously subject to alkylation with the formation of simple carboxymethyl ethers.

In addition to organic acids, their anhydrides can also be considered. For example, in work [161], hot pressing of hydrothermally treated wood was carried out in the presence of acylating agents (maleic and phthalic anhydrides). Hydrothermal treatment disrupts the cellular structure of wood, inducing significant chemical transformations. Subsequent hot pressing with anhydrides increases the strength and moisture resistance of board materials, which is confirmed by studies using chemical analysis and IR spectroscopy. The results showed that the intensity of the bands in the region of 1735–1750 $cm^{-1}$ increased significantly for board materials obtained in the presence of phthalic and maleic anhydrides. The spectra of board materials with phthalic anhydride also contain bands in the region of 770–735 $cm^{-1}$, indicating the presence of 1,2-disubstituted benzene derivatives.

There are different opinions about the modifying role of urea. Several researchers [162] attribute wood modification by urea primarily to polycondensation processes involving urea, lignin, and the readily accessible hemicellulose fraction. Studies have shown that the interaction of birch wood, subjected to hydrothermal treatment with urea during hot pressing, results in wood composites that are notably stronger than those produced industrially.

IR spectroscopy was used to study wood samples subjected to hydrothermal treatment before and after hot pressing in the presence of urea. When comparing the IR spectra, a decrease in the intensity of the absorption bands in the region of 3400 and 1720 $cm^{-1}$ was observed for the samples pressed with urea compared to the samples subjected to hydrothermal treatment. This indicates that the reaction of urea occurs at the -OH and C=O groups of the wood components. In the IR spectra of the materials pressed with urea, all three absorption bands corresponding to Amid-I, Amid-II, and Amid-III are observed: 1660 $cm^{-1}$—vibrations of the carbonyl group in urea derivatives, 1630 $cm^{-1}$—composite frequencies of NH and CN vibrations of the primary amino groups— Amid-II; 580 $cm^{-1}$ is the band corresponding to Amid-III [162].

Article [163] presents the results of research devoted to studying the effect of pre-treatment of birch wood and the use of hydrogen peroxide to accelerate the hydrolytic processes occurring during hot pressing without the use of binders in the production of composite materials. The results showed that the dependence of the values of the dynamic modulus of elasticity and the strength of the material under static bending on the amount of hydrogen peroxide introduced is extreme.

Hydrogen peroxide affects the rate of wood hydrolysis during explosive autohydrolysis, thereby altering the physical and mechanical properties of the final composite. The amount of peroxide, temperature, and duration of treatment determine the density, strength, water absorption, and swelling of the material. An initial increase in peroxide dosage improves properties, but excessive amounts cause negative changes. Hydrogen peroxide's advantage lies in its instability: during high-temperature treatment, it decomposes into harmless components, reducing the risk of adverse effects during use [149].

Fenton's reagent is a mixture of an iron-containing salt and hydrogen peroxide; the decomposition of peroxide in the presence of iron ions generates hydroxyl radicals. Particles and fibers of plant material can be pre-treated with a special compound that makes their surface more active and allows for the formation of more chemical bonds. During the reaction, iron helps convert the peroxide into active particles—hydroxyl radicals. These radicals create additional active sites in the lignin structure, enhancing the performance of the final material [89,142].

Analysis of the results of studies conducted on the chemical modification of various lignocellulose-containing raw materials with the aim of intensifying the processes of obtaining BFC provides the foundation for future, more in-depth studies employing advanced research methods. The DSC method has become a key stage in the research and analysis of chemical processes for the modification of lignocellulose-containing raw materials, aimed at studying the formation of BFC [156].

When studying [164], the formal kinetics of the process using the DSC method in closed crucibles, thermal effects were identified (Fig. 17): an endothermic minimum (≈210°C) and an exothermic maximum (≈320°C).

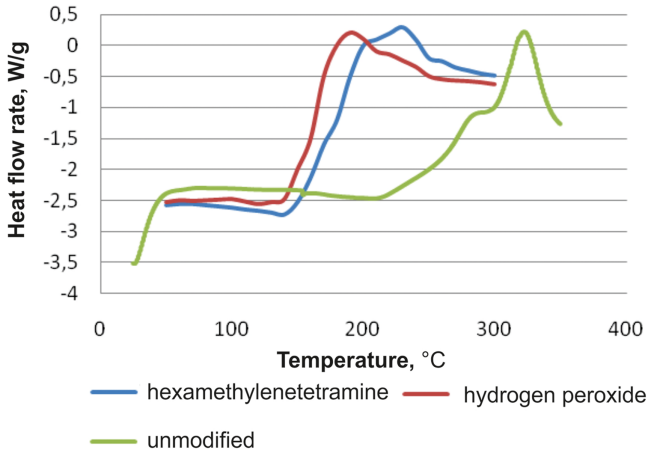


**Figure 17:** Dependence w = f(T) for pine sawdust (humidity—12%, modifiers—hydrogen peroxide, urotropine) in closed crucibles at a heating rate of 20°C/min in a nitrogen atmosphere [164].

The endothermic minimum reflects the hydrolysis of the lignin-carbohydrate complex and easily hydrolyzed cellulose (polysaccharides). The exothermic maximum corresponds to polycondensation processes leading to the formation of BFC. This process is catalyzed by acids formed during wood pyrolysis, as well as by resin acids contained in extractives. Thus, this process can be considered a nth-order reaction with autocatalysis.

For pine sawdust with modifying additives (hydrogen peroxide and urotropine), the peak maxima on the DSC curves shift to the left, which indicates that these compounds act as catalysts for the above processes (≈100°C–120°C and ≈180°C–220°C), accelerating the process of hydrolysis of wood polysaccharides, as well as the lignin-carbohydrate complex.

The use of hydrogen peroxide accelerates the first stage of the process more than fourfold compared to the modification of the pressed raw material with urotropine. A similar trend is also observed in the second stage of the process.

According to the total time of formation of the BFC, the activity of the molding material under consideration can be arranged in the following order: (unmodified molding material) > (molding material modified with urotropin) > (molding material modified with hydrogen peroxide) [164].

Using the DSC method, a study was carried out [156] on the influence of humidity and chemical modifiers in the production of plant binder-free composites based on wheat husk (Fig. 18).

During the initial stage of composite formation, the unmodified molding composition (12% moisture) exhibited the lowest activation energy, amounting to 89.5 kJ/mol. The highest activation energy was found for the modified molding composition with 12% moisture content and 5% hydrogen peroxide consumption, amounting to 140 kJ/mol. In the second stage of the composite formation process, the modified composition with 0.1% hydrogen peroxide had the lowest activation energy, amounting to 83 kJ/mol.

The introduction of hydrogen peroxide into the molding composition leads to an increase in activation energy, which is due to its initial decomposition process. The resulting functional groups subsequently actively participate in the formation of the BFC [156].

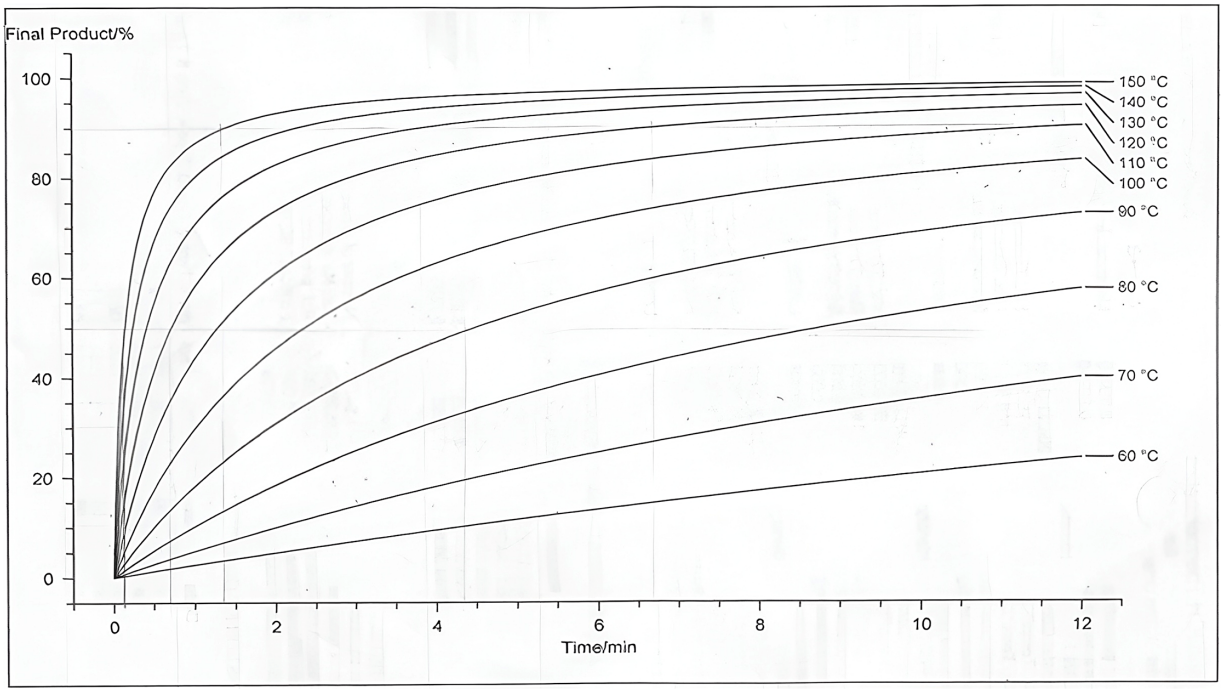


**Figure 18:** Dependence of the degree of conversion on time at different temperatures (wheat husk, modifier—hydrogen peroxide, initial moisture content of the molding material—12%) [156].

Delignification of wood raw materials in an acidic environment in the presence of hydrogen peroxide requires the use of catalysts. For example, transition metal compounds (molybdenum, tungsten) react with hydrogen peroxide to form intermediate peroxo complexes, which transfer active oxygen from hydrogen peroxide to an organic acid [165].

Background on glass transitions of wood components and their moisture dependence is available [166].

In the work [55], a mixture of hydrogen peroxide and manganese-containing sodium vanadomolybdophosphate (MVMP) with the gross formula Na11 [PMo6V5O39Mn(OH)] was used for the chemical activation of lignin in order to obtain composite from wheat husk and pine sawdust. To study the formal kinetics of chemical reactions of wheat husk and pine sawdust lignin in the presence of hydrogen peroxide and MVMP, heat flux measurements were carried out in closed steel crucibles using the DSC method.

Analysis of kinetic dependencies according to Friedman (Fig. 19) indicates that the process of hydrothermal destruction of the lignin-carbohydrate complex is quite complex (as evidenced by the inconsistency of the activation energy depending on the degree of conversion).

Therefore, formal kinetics was used to calculate the kinetic parameters using dependencies for 1st-order, 2nd-order, n-order, and n-order reactions with auto acceleration. The best model is a 2nd-order reaction. The graphical solution is shown in Fig. 20, and the kinetic parameters are presented in Table 4.

Similar calculations were performed using the DSC curves at the composite formation stage (Fig. 21). The formal kinetics of composite production based on pine sawdust were similarly studied. The results are presented in Table 4.

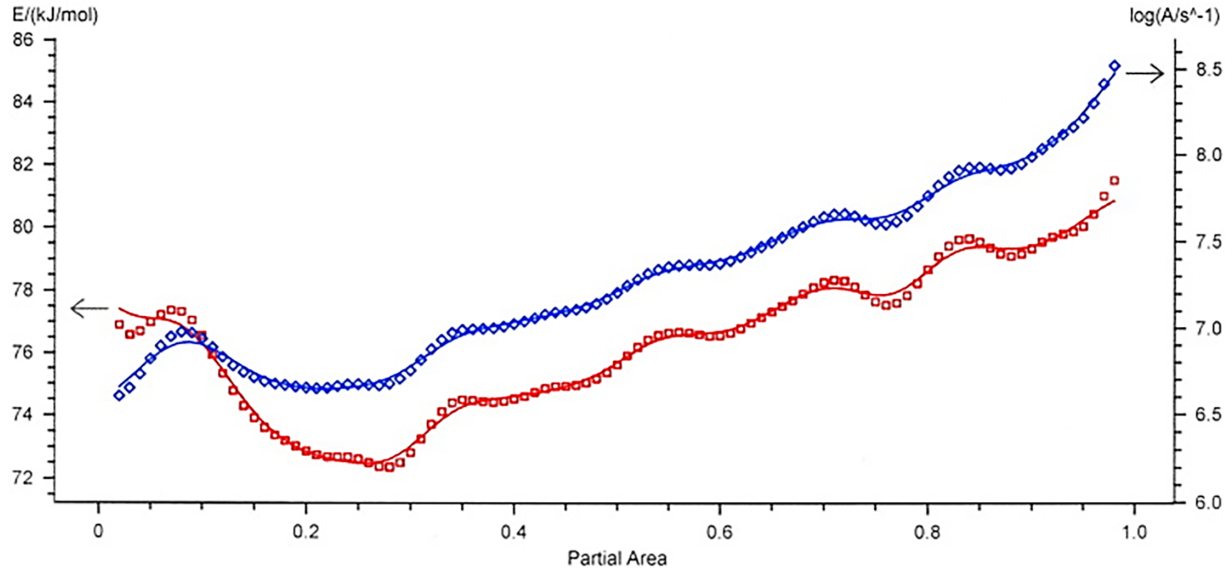


**Figure 19:** Friedman isoconversional results for the hydrothermal destruction stage: effective activation energy E (red squares, left axis) and log(A, $s^{-1}$) (blue diamonds, right axis) as functions of conversion alpha (shown as partial area) [156]. Kinetic parameters for different compositions are summarized in Table 4.

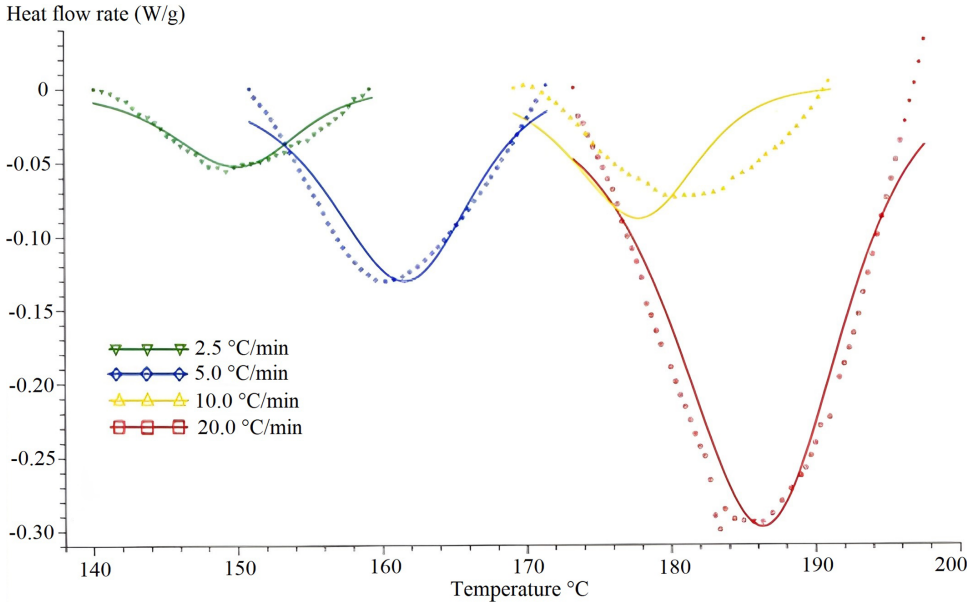


**Figure 20:** Dependences of heat flow on temperature for a second-order reaction during hydrothermal destruction of a lignin-carbohydrate complex (initial moisture content of the molding material in the form of wheat husk—16%, hydrogen peroxide consumption—6% (wt.), MVMFN consumption—6%) at different heating rates 2.5; 5.0; 10.0; 20.0 (°C/min). DSC curves: solid lines—calculated values, dots—experimental [156].

**Table 4:** Kinetic parameters of the process of formation of BFC [156].

| No. p/p | Indicator | Wheat Husk | | Sawdust Pine Trees |
|---|---|---|---|---|
| | | 1% $H_2O_2$ $W$ = 8% | 6% $H_2O_2$ $W$ = 16% | 1% $H_2O_2$ $W$ = 16% |
| The first stage of the process (hydrothermal destruction of the lignocellulosic matrix) | | | | |
| 1 | Pre-exponential factor lg $A_1$, $c^{-1}$ | 3, 54 | 7, 19 | 5.47 |
| 2 | Effective activation energy $E_1$, kJ/mol | 52, 3 | 82, 1 | 73.1 |
| 3 | Reaction order, $n$ | 0.9 | 1.1 | 1.1 |
| 4 | Correlation coefficient of processes, $r$ | 0.87 | 0.97 | 0.96 |
| The second stage of the process (composite formation) | | | | |
| 1 | Pre-exponential factor lg $A_2$, $c^{-1}$ | 6, 02 | 8, 61 | 6.24 |
| 2 | Effective activation energy $E_2$, kJ/mol | 92, 5 | 115,2 | 93.0 |
| 3 | Reaction order, $n$ | 3, 1 | 2.9 | 1.5 |
| 4 | Correlation coefficient of processes, $r$ | 0.94 | 0.95 | 0.92 |

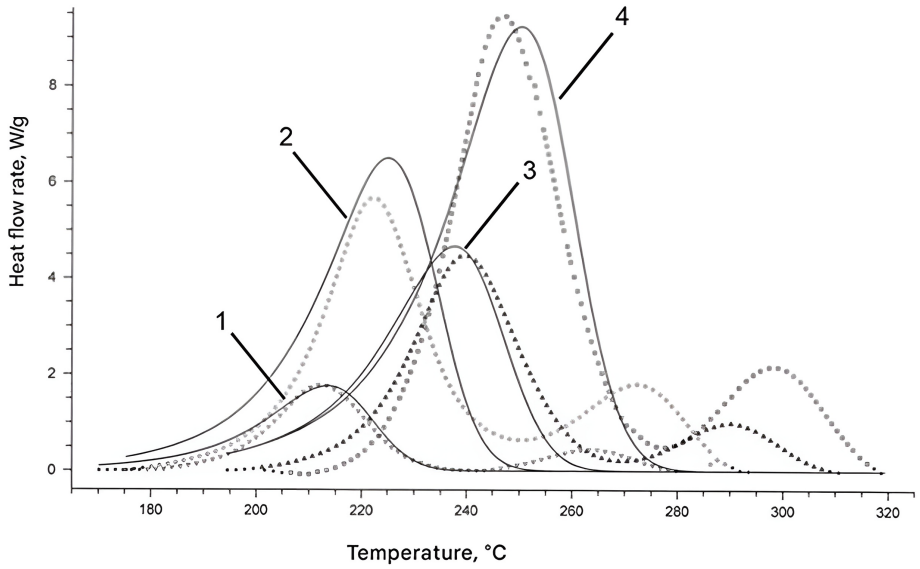


**Figure 21:** Dependences of heat flow on temperature for the second-order reaction at the stage of formation of BFC based on wheat husk (initial moisture content of the molding material W—16%, hydrogen peroxide consumption—6% (wt.), MVMFN consumption—6%) at different heating rates (°C/min): 1—2.5; 2—5.0; 3—10.0; 4—20.0 (DSC curves: solid lines—calculated values, dots—experimental) [156].

The rate of the hydrothermal destruction of the lignin-carbohydrate complex and the stage of formation of the BFC depend not only on the consumption of hydrogen peroxide but also on the chemical structure of lignin (Table 4).

This can be explained by the fact that wheat straw lignin is composed of three types of subunits (HGS). Their reactivity towards ozone differs significantly, decreasing in the order S → G → H [167].

Studies of the formal kinetics of composite production show that lignin from coniferous trees has a higher reactivity than lignin from annual plants. These results are consistent with the results on the oxidation of model compounds of lignin from coniferous, deciduous trees, and plant-derived lignin [168,169], as well as with the results of quantum chemical calculations [130,135,136,138].

Thus, the choice of modifier depends not only on the type of plant material used, but also on the conditions of its hot pressing and the required physical and mechanical properties of the resulting material.

## 7 Summary and Prospects

Binder-free lignocellulosic boards provide a pathway to reduce formaldehyde-related concerns and increase circularity, yet industrial scale-up is still limited by three coupled challenges:

- moisture sensitivity (swelling and loss of strength);
- energy intensity of pretreatment and pressing;
- feedstock variability that compromises reproducibility.

Future studies should shift from descriptive reporting toward quantifiable structure–property models. Priority directions include:

- *in situ* monitoring of bond formation during pressing (thermal analysis and spectroscopy) to link chemical transformations to internal bond strength and bending performance;
- controlled activation chemistries that lower required pressing severity while maintaining biodegradability and low toxicity (oxidant- or nitrogen-assisted routes compatible with closed-mold processing);
- moisture-management design (severity tuning, press closing schedules, and venting strategies) to balance bond development with dimensional stability;
- standardized reporting of feedstock descriptors and processing parameters (particle morphology, sealing degree, moisture gradients) to enable inter-study comparability.

Overall, progress will require integrating advances in lignin chemistry with process engineering so that mechanistic hypotheses translate into predictive manufacturing windows for specific product classes (construction, packaging, insulation).

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